Pressure Induced Quantum Critical Point and Non-Fermi-Liquid Behavior in $BaVS_3$

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The phase diagram of $BaVS_3$ is studied under pressure using resistivity measurements. The temperature of the metal to nonmagnetic Mott insulator transition decreases under pressure, and vanishes at the quantum critical point $p_{\rm cr}$ = 20kbar. We find two kinds of anomalous conducting states. The high-pressure metallic phase is a non-Fermi liquid described by $\Delta\rho \propto T^n$ where n =1.2–1.3 at 1K< T <60K. At $p < p_{\rm cr}$, the transition is preceded by a wide precursor region with critically increasing resistivity which we ascribe to the opening of a soft Coulomb gap.

Understanding the Mott transition, and clarifying the nature of the phases on either side of the transition, is a matter of great importance. Though metal–insulator transitions are often accompanied by an ordering transition and/or influenced by disorder, one may speak about a "pure" Mott transition which is a local correlation effect in an ideal lattice fermion system, and takes place without breaking any global symmetry. Many aspects of this problem can be studied on the multifaceted behavior of $BaVS_3$ [1–3].

The metal–insulator transition of the nearly isotropic 3D compound $BaVS_3$ offers a realization of the pure Mott transition in nature [3]. Under atmospheric pressure $BaVS_3$ has three transitions: the hexagonal-to-orthorhombic transition at T_S = 240K which has only a slight effect on the electrical properties; the metal–insulator transition at $T_{\rm MI}$ = 69K, which does not seem to break any of the symmetries of the metallic phase; and the ordering transition at T_X = 30K [4]. In spite of decades of effort, the character of the phases and the driving force of the transitions at $T_{\rm MI}$ and T_X, remain mysterious.

Here we report the results of single crystal resistivity measurements under hydrostatic pressure in the range of 1bar $\leq p <$ 25kbar. These pressures encompass the entire insulating phase and part of a high-pressure low-T conducting phase. We report the first observation of the quantum critical point in $BaVS_3$, and we characterize the strange metallic phase lying beyond the critical pressure $p_{\rm cr}$. On the metallic side of the phase boundary, we identify two regimes with anomalous properties: (i) a broad region at $p < p_{\rm cr}$ in which the resistivity increases strongly with decreasing temperature, and (ii) a high-pressure non-Fermi-liquid state.

Single crystals of $BaVS_3$ were grown by Tellurium flux method. The crystals, obtained from the flux by sublimation, have typical dimensions of 3 × 0.5 × 0.5 mm^3. The resistivity was measured in four probe arrangement. The current was kept low enough to avoid the self-heating of the sample. For the high-pressure measurements the crystal was inserted into a self-clamping cell with kerosene as a pressure medium. The pressure was monitored in-situ by an InSb sensor. During cooling down the cell there was a slight pressure loss, but its influence on the temperature dependence of the resistivity was negligible. Above about 15 kbar the pressure was stable within 0.1 kbar in the whole temperature range.

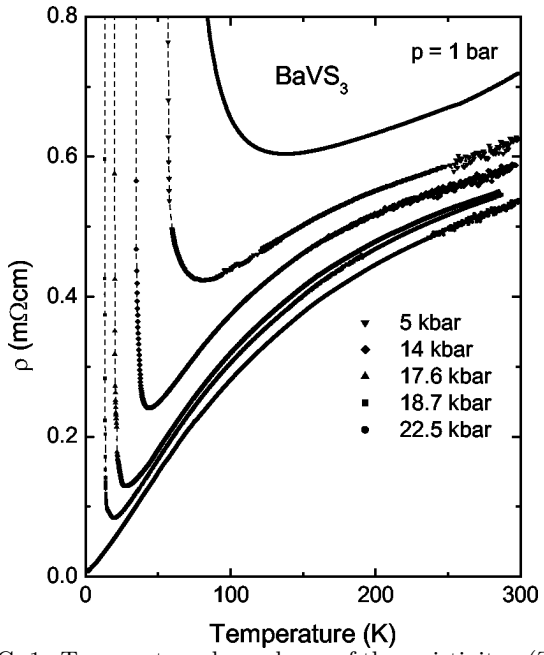

FIG. 1. Temperature dependence of the resistivity $\rho(T)$ for various pressures. The T = 0 insulator-to-metal transition sets in at $p_{\rm cr}$≈20kbar.

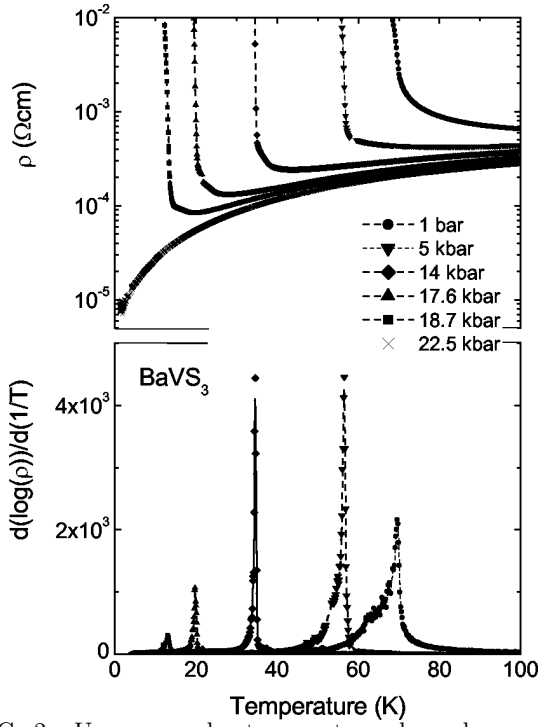

FIG. 2. Upper panel: temperature dependence of the resistivity $\log \rho(T)$ for various pressures. Lower part: $d \log \rho / d(1/T)$ for selected pressures. The spikes define the metal–insulator transition temperatures.

Figure 1 shows the temperature dependence of the resistivity for various pressures. As expected from earlier low-pressure data [1], $T_{\rm MI}$ decreases smoothly with increasing pressure. The linear plot highlights the contrasting behavior of $\rho(T)$ below and above the critical pressure, but does not include the regime of higher resistivities. Part of this is shown in the logarithmic plot of Fig. 2; it can be perceived that the overall resistivity change at the transition remains roughly the same, though $T_{\rm MI}$ is suppressed. The pressure dependence of the metal–insulator transition temperature was determined from the spikes of the logarithmic derivative, $d(\log \rho)/d(1/T)$, as shown for selected pressures in the lower panel of Fig. 2. The narrowness of the spikes demonstrates that the transition remains sharp under pressure. For $p = 19.8$kbar we still found a metal–insulator transition at $T_{\rm MI} \approx 5.6$K, but for 21.4kbar, the resistivity keeps on decreasing at least down to 1K. We estimate that $p_{\rm cr} \approx 20$kbar. The phase boundary is shown in Fig. 3. Our resistivity measurements allow the division of the conducting phase into further regions of markedly different nature; the discussion of these follows.

For $p < p_{\rm cr}$ the resistivity in the metallic phase has a marked minimum at $T_{\rm min}(p)$ preceding the metal–insulator transition. Finding $d\rho/dT < 0$ in a metal is anomalous, and it is tempting to regard the interval $T_{\rm MI} < T < T_{\rm min}(p)$ as an extended precursor regime to the insulating phase. As shown in Fig. 3 by the dashed line, $T_{\rm min}$ drops to zero simultaneously with $T_{\rm MI}$: the insulator and its precursor vanish together. We believe that the resistivity minimum is a collective effect; if it were due to impurities, it would have no reason to disappear beyond $p_{\rm cr}$.

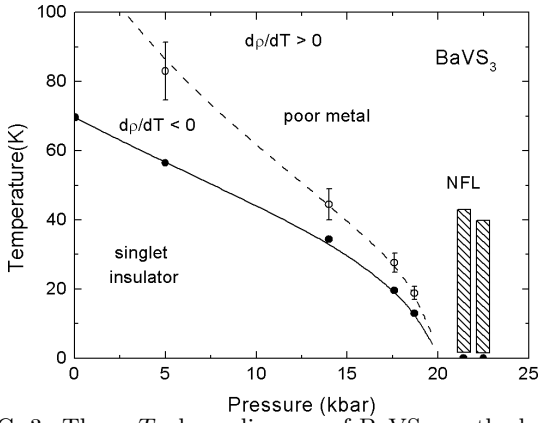

FIG. 3. The p–T phase diagram of $BaVS_3$ on the basis of resistivity measurements. Solid line: metal–insulator phase boundary, dashed line: the boundary of the precursor region. The columns indicate the range of the non-Fermi-liquid $\Delta\rho \sim T^n$ law.

$BaVS_3$ is essentially an isotropic 3-dimensional system [3], thus the appearance of a wide precursor regime within the metallic phase is not a regular feature. There is, however, an interesting subclass of Mott systems to which it is common: e.g., similar behavior is seen above the Verwey transition in magnetite [5,6]. The $T_{\rm min}(p)$ line does not have the significance of a phase boundary; it merely marks the temperature where fluctuations towards a gapped state become so strong that they determine the sign of $d\rho/dT$. The Hall results on polycrystalline $BaVS_3$ [2] imply that the number of carriers changes in this temperature range, and we believe that resistivity enhancement arises from the loss of charge carriers. A phenomenon of this nature is observed in Fe_3O_4, where increasing charge short range order results in a diminishing effective number of carriers, and a resistivity minimum [6].

It is remarkable that the apparent opening of a soft charge gap is not accompanied by the opening of a spin gap; the magnetic susceptibility does not show any noticeable anomaly at $T = T_{\rm min}$ [3]. This suggests that the phenomenon which sets in at $T_{\rm min}$ is quite distinct from the opening of a real gap which happens at $T_{\rm MI}$. $T_{\rm min}(p)$ can rather be associated with the onset of charge short range order, and the appearance of a soft charge gap which has no effect on the magnetic properties. We note that a somewhat similar scenario, but with particular emphasis on possible 1D aspects, was considered in [2]. However, the essentially isotropic conductivity [3] rules out 1D interpretations.

The resistivity data suggest that the insulating state is approached through a regime of critically increasing resistivity. There are precedents that valuable insight into

the nature of phase transitions in strongly correlated systems can be gained by trying to identify critical behavior in transport data [7]. The critical behavior can be demostrated by plotting the resistivity, $\rho(t)$, as a function of the reduced temperature on logarithmic scales ($t = (T - T_{\rm MI})/T_{\rm MI}$). The ambient pressure result is shown in Fig. 4: the power law $\rho \propto t^{-0.4}$ gives a good approximation over more than 30 K above $T_{\rm MI}$, over almost 2 decades in the reduced temperature, t.

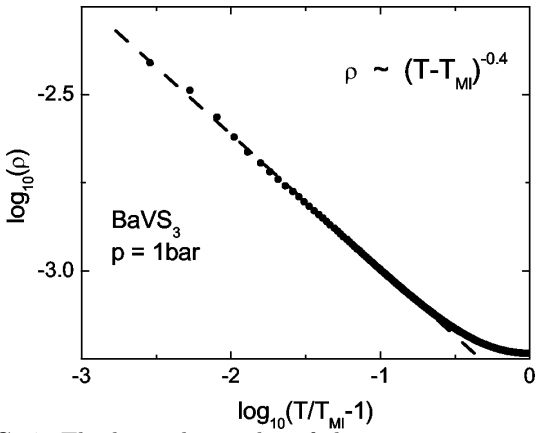

FIG. 4. The logarithmic plot of the resistivity vs reduced temperature. The resistivity follows a power law in a substantial part of the interval $T_{\rm MI} < T < T_{\rm min}$.

Phenomenologically, low-pressure $BaVS_3$ can be related to other (essentially 3D) systems which share at least some of its relevant features: the existence of the intermediate disordered insulating phase, the resistivity precursor, and the lack of a discernible Fermi edge in XPS spectra [8]. In addition to magnetite [5,6] we mention Ca_2RuO_4 [9], and Ti_4O_7 [5]. The detailed behavior of either of these systems is quite different from that of $BaVS_3$, but we believe that there is also a common feature: the soft Coulomb gap due to short-range charge fluctuations.

Next we discuss the high-pressure metallic phase. Figure 5a reveals that the temperature dependence of the resistivity is characteristic of a bad metal [10]. The high temperature behavior is sub-linear, and though $\rho(T = 300{\rm K})$ corresponds to a mean free path $l \sim$5–8Å, which is of the order of the lattice constant, ρ continues to grow without any sign of saturation. It has been shown that strong electron–phonon scattering could account for such a behavior [11], but we believe that in our case the electron–electron scattering dominates. This assumption is supported by the specific heat data [12]: the electronic (primarily orbital) entropy keeps on increasing even beyond 300K. The magnitude and the unusual shape of $\rho(t)$ indicate a new scattering process, which is to be associated to orbital fluctuations.

The low temperature region of the pressure-induced metallic phase is particularly interesting. For $T < 60$K the resistivity does not follow the characteristic Fermi liquid behavior $\Delta\rho = \rho(T) - \rho_0 \propto T^2$ (ρ_0 is the residual resistivity). Furthermore, the log–log plot of $\Delta\rho(T)$ is approximately linear in an extended range, allowing to fit the resistivity with the customary non-Fermi-liquid 'law' $\Delta\rho \propto T^n$, where in general $1 \leq n < 2$ [13]. Figure 5b shows that $\Delta\rho \propto T^{1.25}$ gives an excellent description for $BaVS_3$ for 1K$< T <$50K. A somewhat larger temperature range with $n \approx 1.2$ is found at $p = 21.4$kbar. The extent of the non-Fermi-liquid regime is given by columns in Fig. 3.

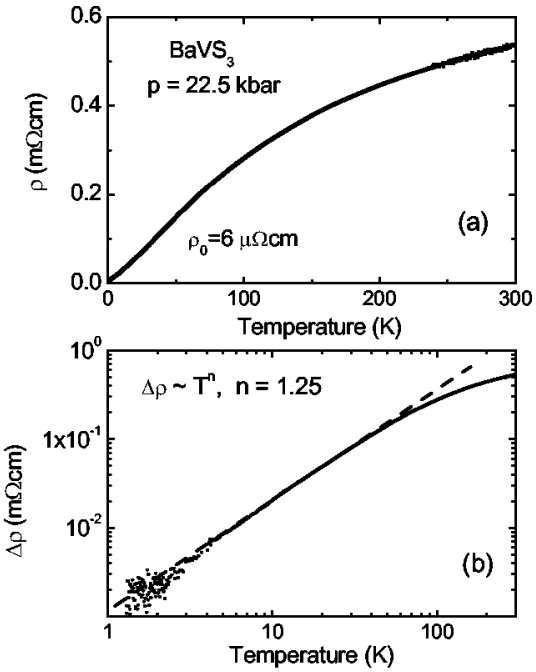

FIG. 5. a) The temperature dependence of the resistivity at $p = 22.5$kbar on linear scales (a), and of $\Delta\rho = \rho - \rho_0$ on logarithmic scales.

The above low temperature behavior is similar to that of nearly antiferromagnetic f-electron systems such as $CePd_2Si_2$ [14]. The interpretation usually invokes nearness to a quantum critical point, or the existence of rare regions [13,15,16]. In these cases the non-Fermi-liquid region is placed into a phase diagram where the static properties of the phases are in principle well understood. It is not so with $BaVS_3$ for which there is no consensus either about the driving force of the metal–insulator transition, or the nature of the low-T phases. Since even weak extrinsic disorder can have a drastic effect on the critical behavior, the relative importance of correlation and disorder should also be considered both for the insulator and the various conducting regimes.

The effects of the vicinity of a ferromagnetic, or an antiferromagnetic, quantum critical point on the metallic resistivity have been worked out [13]. The overall appearance of the susceptibility curve [3] shows that $BaVS_3$ is dominated by antiferromagnetic spin–spin interactions, so the predictions concerning the resistivity of a nearly antiferromagnetic metal are relevant. It has been argued that for samples of sufficiently good quality, $\Delta\rho \propto T^n$

where $n < 1.5$, and finding $n = 1.2$–1.3 over 1–2 decades of T is a reasonable expectation [17]. This is in full accordance with our results. The fact that at $p = 22.5$kbar $\rho_{300}/\rho_0 \sim 100$, shows that our sample is of good quality and disorder effects are weak as far as the high-pressure conductor is concerned.

Let us note here that $CaRuO_3$ provides another example of a d-electron system whose non-Fermi-liquid nature is probably explained by its being nearly antiferromagnetic. However, its resistivity follows the $\Delta\rho \propto T^{1.5}$ relationship [18], which is expected for dirty samples [17].

The reason for the lack of magnetic long range order in the $T_X < T < T_{\rm MI}$ insulating phase is not evident. One may first think that the in-plane frustration is responsible because the V ions form triangular a–b planes. However, neither the isotropic nor the anisotropic triangular Heisenberg model is, for any spin, frustrated enough to give a spin liquid [19]. Here one may be tempted to invoke disorder: it is known that quantum antiferromagnets (especially for $S = 1/2$) tend to be unstable against the formation of a random singlet phase [20]. The theoretical issue is still open, but the outcome that antiferromagnetism should be always unstable against quenched disorder, is considered implausible [16].

We believe that in a weakly frustrated system like $BaVS_3$, the Heisenberg model would order, and $BaVS_3$ is non-magnetic because its effective hamiltonian is not a pure Heisenberg model. We argued in Ref. [3] that including the orbital degrees of freedom of the low-lying crystal field quasi-doublet, one finds a large number of energetically favorable dimer coverings of the triangular lattice such that intra-dimer spin coupling is strong, while inter-dimer perturbations are weak. The equilibrium phase at $T_X < T < T_{\rm MI}$ can be visualized as a thermal average over a class of valence bond solid states. Intra-dimer interaction causes the opening of a spin gap, while inter-dimer interactions results intermediate-range correlation, and a $\mathbf{Q}$-dependence in the spin excitation spectrum [21]. In this model we do not have to invoke disorder to explain the singlet phase. Quite on the contrary: either sulfur off-stoichiometry [22], or Ti-doping [23], is known to break up singlet pairing. The well-developed singlet insulating phase is the hallmark of a clean system.

In conclusion, we studied the phase diagram of the non-magnetic Mott system $BaVS_3$ by resistivity measurements. A quantum critical point $p_{\rm cr} \approx 20$kbar was found, and the results revealed the existence of anomalous conducting regimes. The pressure-induced metallic phase is a non-Fermi-liquid at $T < 60$K. We suspect that at high temperatures the electrical transport is determined by the scattering on orbital fluctuations. For $p < p_{\rm cr}$ an unusually wide precursor regime was identified above the metal–insulator transition. In this regime, which is attributed to the appearance of a soft charge gap, $\rho(t)$ can be well described by a power law of the reduced temperature. The microscopic nature of these regimes remains to be elucidated.

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